# REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-01-

0130



| | | |
|---|---|---|
| **1. REPORT DATE** *(DD-MM-YYYY)*<br>10/01/01 | **2. REPORT TYPE**<br>Final Progress Report | **3. DATES COVERED** *(From - To)*<br>06/01/97 - 05/30/00 |

**4. TITLE AND SUBTITLE**
Re-Writable Two-Photon Three dimensional Optical Memory

**5a. CONTRACT NUMBER**

**5b. GRANT NUMBER**
AFOSR F 49620 97 10454

**5c. PROGRAM ELEMENT NUMBER**

**6. AUTHOR(S)**
Dr. Paras N. Prasad

**5d. PROJECT NUMBER**

**5e. TASK NUMBER**

**5f. WORK UNIT NUMBER**

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**

Research Foundation of SUNY,
PO Box-9,
Albany, NY-12201-0009.

**8. PERFORMING ORGANIZATION REPORT NUMBER**

**9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)**

AFOSR/NL
801 N. RANDOLPH ST, ROOM 732
ARLINGTON, VA 22203-1977

**10. SPONSOR/MONITOR'S ACRONYM(S)**

**11. SPONSOR/MONITOR'S REPORT NUMBER(S)**

**12. DISTRIBUTION / AVAILABILITY STATEMENT**

Approved for Public Release: Distribution Unlimited



**13. SUPPLEMENTARY NOTES**

**14. ABSTRACT**

Using a polymer block, doped with a highly efficient two-photon dye, we have achieved a high density data-storage with gray-scale control in multiple planes as stacked Compact Disks (CDs) at a separation of 10 μm. The absorption and fluorescence of the dye at the written spot shift to a longer wavelength, permitting an easy fluorescence mode readout with a linear excitation using an inexpensive laser source. The storage capacity in this case is estimated to be $10^{12}$ bits/cm$^3$. To demonstrate the practical use of this technology, a three dimensional barcode writer / reader system was developed. We were able to write multiple layers of barcodes in a dye doped polymer media using highly localized two-photon process and were able to read the barcodes using a scanning laser beam coupled with confocal detection of single photon fluorescence.

**15. SUBJECT TERMS**

| **16. SECURITY CLASSIFICATION OF:** | | | **17. LIMITATION OF ABSTRACT** | **18. NUMBER OF PAGES** | **19a. NAME OF RESPONSIBLE PERSON** |
|---|---|---|---|---|---|
| **a. REPORT**<br>Unclas | **b. ABSTRACT**<br>Unclas | **c. THIS PAGE**<br>Unclas | | 10 | **19b. TELEPHONE NUMBER** *(include area code)* |

The need for data storage is explosive, triggered by the development of multimedia and electronic communication networks which is expected to cross $10^{20}$ bits/storage media, by year 2000. Due to this astronomical increase in the requirement of data storage, intense research activity is going on to find alternate methods and storage media for such large amounts of data. Recently the focus has shifted from the two dimensional storage to three dimensional storage. Several approaches to three-dimensional (3D) optical data storage, such as, holographic recording with photorefractive media,[1-3] hole burning,[4] and photon echo,[5] are currently being investigated. The use of two-photon processes for optical data storage was first introduced by Rentzepis.[6-8] and subsequently by Webb[9]. Since then there have been several reports also proposing the use of two-photon processes for optical data storage.[10-13]. The advantages of two-photon based memory systems are, (1) volume storage with high data storage densities of the order of $10^{12}$ bits/cm$^3$, (2) fast read/write times, (3) random access, and (4) low cost storage media. As the two-photon excitation has a quadratic dependence on the pump intensity, the excitation and subsequent photoreaction related to the writing process occurs only in the near vicinity of the focal point. An excellent z resolution during the writing process is possible due to this property of two-photon induced processes. In a polymer doped with a chromophore, an infrared beam can penetrate deeper than visible light, due to a very low linear absorption at longer wavelength and inherent low absorption due to the two-photon process. The basic components of a two-photon memory are, a medium which exhibits a change in its optical properties (absorbance, fluorescence, refractive index, etc) after two-photon absorption, appropriate read and write beams, and a mechanism to precisely access any volume element in the medium. We have already demonstrated the 3D data storage using a two photon confocal microscope (read and write)[13]. In this paper we demonstrate data storage based on two-photon induced shift of the spectral properties of a dye which permits the use of a simple low power and inexpensive CW laser for read back, avoiding the usage of complicated and expensive pulsed laser system for read back.

A new dye was used which is a highly efficient two-photon absorber, producing a strong up-converted emission. At higher peak intensity, the two photon induced photochemical process shifts the absorption and fluorescence of the written region to a

longer wavelength. The read back can therefor be done either in two-photon excitation mode using a pulsed IR beam or in a single-photon excitation mode using a CW laser like Kr/Ar laser. The data storage is in the form of stacked CD arrangement, i.e., in multiple layers with storage capacity exceeding terabits per cubic centimeter. Although the method can be used for both for digital and analog storage but in this case we use a digital bitmap for storage but demonstrates gray scale control.

For data writing, the excitation beam was generated by a mode-locked Ti:Sapphire laser oscillator pumped by an argon-ion laser. This system produced a train of 798 nm pulses of duration 70 fs each, at a repetition rate of 90 MHz. Although the average beam power was 200 mW, it was attenuated such that the maximum power measured at the sample was less than 40 mW. In later stages, this laser system was replaced by a commercial Ti:Sapphire laser (Tsunami from Spectra Physics) pumped by a DPSS laser (Millennia also from Spectra Physics).With this new laser also, pulse width, repletion rate and power used were similar to that mentioned for old laser. An efficient data writing system was developed using a motorized X-Y stage, and a galvanometer mirror shutter. The laser beam was focussed on to the sample using a 60X oil immersion objective lens attached to a computer-controlled vertical translator for focus control. A commercial confocal laser scanning microscope (Biorad MRC-1024) with a 60X oil immersion lens (numerical aperture 1.4) was used for reading the data, in both one photon and two photon excitation modes. For two photon read back the same Ti:Sapphire laser was used with a lower intensity (~10-20mw average power) while for one photon detection the 514nm line of the Argon laser was used. As one photon read back can be done with any wavelength in the range of 470-520nm, one can use 488nm line from Kr:Ar laser or even a compact solid state lasers which are now available in the market. To demonstrate this, we have also used the 488nm line of Kr:Ar laser for read back.

**Storage Media:**

A PMMA (poly-methyl methacrylate) polymer block doped with the new two-photon chromophore (2% by weight) AF240 (7-benzothiazol-2-yl-9,9 diethylfluoren-2-yl)diphenylamine), obtained from the polymer branch of the US Airforce Research Laboratory, was used as the data storage medium. When a focused infrared beam from the Ti:Sapphire laser is incident in the sample, there is a strong two-photon induced green

fluorescence at the focal point. In case of PMMA blocks, the dyes were dissolved in the monomer (MMA) and then it was polymerized to get the dye doped polymer block . Instead, we can also use many kind of polymer sheets(eg., poly-ester, poly-ethylene) and then the dye can be infiltrated into the sheet using dye solution(A new technique has been developed for this). As the change in fluorescence is a property of the dye, we can use any kind of organic or inorganic matrix to incorporate dye. This way the choice of storage medium is flexible.

Further the choice of dye also is flexible as any dye with good two-photon absorption and show change in the fluorescence properties after two-photon absorption, can be used for this purpose. From a series of dyes ( AF 240 is a member of this series) developed at Airforce Research Laboratory at Dayton, most of the dyes had this property at varying levels. Similarly, some dyes developed in our laboratory (eg., APSS 4-[N-(2-hydroxyethyl)-N-methyl) amino phenyl]-4′-(6-hydroxyhexyl sulfonyl)stilbene ) also shows similar properties at a lower level.

The chromophore AF240, show new absorption and emission peaks upon continued two-photon excitation ( at 800 nm) above 40 mw. The same spectral changes can be induced be exposure to UV light ($\leq$ 400 nm). Fig.1 shows the absorption and fluorescence spectra before and after exposing a PMMA film, doped with AF240, to strong UV light for more than 2 hours . It can be seen from the absorption curve that the absorption peak at 400nm gets suppressed and another small peak starts appearing at 500nm after continuos exposure to the UV light. Similarly, the fluorescence spectra of the film after exposure to the UV (Fig. 1) shows the appearance of emission at 570 nm when excited at 500nm. A similar process occurs after intense two-photon excitation at 800 nm, the exposed regions show reduced fluorescence by two-photon excitation at 800nm. The phtotolized material exhibits fluorescence at 570 nm when linearly excited with the 514nm line of Argon ion laser. Although, we are still trying to understand the exact nature of the photoprocess, change in the excitation and emission can be used for a read back mechanism in both the two-photon and the single photon excitation modes. In read back using single photon excitation, the written regions appear as bright compared to the dark background while in read back using two-photon excitation the

written regions appear as dark compared to the background. Each of them have their own advantages. For example, the two photon read back has a high axial resolution while single photon read back produce a higher contrast and is much simpler in implementation.

A series of images separated by 6 μm in the z direction (depth), were written in the volume of the polymer block by the two-photon process. This separation of 6 μm did not produce any overlap of different layers (cross-talk) in the two-photon read back process while in single photon read back, a higher separation (~10 μm) between the layers was needed to avoid cross-talk. Fig. 2 shows the read back images in the two-photon mode as well as in the single photon mode. Although the image contrast is very good in the single photon read back, the overlap of different written layers (6 μm apart) is clearly visible. To get an accurate estimate of the axial resolution in our experimental conditions, an X-Z scan of the written region was done and the fluorescence intensity variation was plotted as a function of depth in the sample (Fig. 3). From the graph, the full width at half maximum (FWHM) for two-photon read back was calculated as 2.8 μm while for single photon read back it was 5.3 μm.. Also for good axial resolution using single photon one has to use the confocal aperture while for two-photon detection confocal aperture is not necessary. The lateral resolution in both the read back mechanisms, was 1 μm under our experimental conditions.

Considering the spacing between layers as 10 μm for single-photon read back, the data storage capacity in this case is $2x10^{11}$ bits/ $cm^3$ , assuming that the resolution achieved by us is the upper limit ( though it is possible to go to higher resolution by optimizing the dye concentration and exposure time). Further, more gray levels can be created by controlling the time of exposure during writing. This means that if one can achieve $2^8$ gray levels for each written bit, this will be equivalent to having a data storage capacity of $10^{12}$ bits /$cm^3$. Fig.4 shows the gray levels created in a polymer block by varying the time of exposure at each bit of the written region. Fig.5 shows another example of this technique in which a photograph was written into and read from a polymeric media.

Using this technique we have developed a 3 dimensional barcode writer and reader. To demonstrate this technique we used Poly-methyl methacrylate (PMMA) doped with dye

AF240 (7-benzothiazol-2-yl-9,9-diethylfluoren-2-yl)diphenylamine ) developed at Airforce Research Laboratory at Dayton, as the barcode storage medium. A tightly focussed pulsed IR beam ( A Ti:Saphire laser operating at 800nm with pulse width 80fs and a repetition rate of 90MHz as light source and a high NA objective for focussing) was used to write barcodes in to the dye doped polymer medium mounted on a computer controlled scanning stage. Necessary software and hardware was developed to convert computer generated images or barcodes to be written in to the medium. In case of the dye AF240, the written spot's linear absorption and fluorescence properties are red shifted compared to unwritten region. Here the written spot shows an absorption at 500nm and emission at 570 nm making it possible to use a readback system comprising of 488nm line of argon laser as the excitation source and confocal detection of the emission at 570nm. Similar techniques were used to write barcodes into different polymer/dye composites utilizing change in emission of the dye or two-photon induced polymerization or refractive index changes. Using this technique we were able to write multiple layers of barcodes/images in a single polymer block at a vertical separation of 10 microns, and up to a depth of couple of hundred microns. This can be used to make security identification labels with secret identification codes well concealed deep inside the label.

**Writing and Reading:**

A tightly focussed pulsed IR beam ( A Ti:Saphire laser operating at 800nm with pulse width 80fs and a repetition rate of 84MHz as light source and a high NA objective for focussing) was used to write barcodes in to the dye doped polymer medium mounted on a computer controlled scanning stage. The writing process utilizes two-photon excitation induced fluorescence change of the dye for storing barcodes. In two-photon excitation, simultaneous absorption of two photons at a higher wavelength ( lower energy) occurs which is equivalent to the absorption of a single photon at a lower wavelength (higher energy). For e.g, in case of Dye AF240, simultaneous absorption of two photon occurs at a wavelength 800nm, which is equivalent to the absorption of single photon at 400nm and fluoresces at 490nm. After the two photon excitation, the dye changes its absorption and emission properties to give an emission at around 580nm when excited at around 488nm. Any material which has similar shift in absorption and emission

properties can be used as the storage medium. Further this can be extended to use three photon or any other multi-photon process, as the resolution increases with higher order multi-photon processes. Only draw back in these cases will be the resolution of single photon confocal read back cannot be increased along with the resolution of higher order multi-photon writing. Even sequential two-photon absorption induced optical changes in the media can be used for the same purpose.

Barcodes generated using a commercial software was used as an input into a homebuilt software, which will control the XY stage, focus motor and the laser shutter to write the barcodes into the storage media.

Currently we are using a commercial confocal microscope as the readback system with 488nm line of a Kr:Argon laser as the excitation. This read back system can be custom made for this purpose without using the bulky commercial microscope. Instead of Kr:Argon laser, a commonly available diode laser giving out 980nm light can be frequency doubled to get 490nm excitation for the reader. Reading is done with a galvanometer mirror scanners, which scans the written layer with the excitation light, and detecting the fluorescence signal through a confocal aperture. Different layers of written layers can be selected by focussing the excitation light at different layers, using a focus motor (stepper motor).

A two layer barcodes written into a PMMA block doped with dye AF240 is shown in figure 6.

This technique differs from the currently available barcode writer/reader systems in the following points -

1. Information is not stored on the surface of the media which make the media scratch proof.
2. Multiple layers of barcodes can be written one below another. ( All the current technologies can store information only in two-dimension.)
3. One can customize the excitation and emission wavelengths of the storage media by properly selecting the dyes, which makes the information more secure.

The main bottlenecks in this technique is the speed of writing and the bulky current setup currently being used.

In conclusion, we have demonstrated a three dimensional optical datastorage system based on two-photon writing and single photon confocal reading. We have incorporated grayscale capability into this system, which can eventually increase the storage capacity. We have also demonstrated the storage and retrieval of multiple layers of images, data or even 3D barcodes in this medium.

## References


**1.** P. Gunter, and J-P. Huignard, Ed. *Photorefractive Materials and their Applications I*, Springer-Verlag, Berlin (1988).

**2.** L. Hesselink, and M. C. Bashaw, *Opt. Quantum Electron.* **25**, 611 (1993).

**3.** M. Liphardt, A. Goonesekera, B. Jones, S. Ducharme, J. M. Takacs, and L. Zhang, *Science* **263**, 367 (1994).

**4.** W. E. Moerner, Ed. *Persistent Spectral Hole Burning: Science and Applications* Springer, Berlin (1987).

**5.** R. Kachru and M-K. Kim, *Opt. Lett.* **28**, 2186 (1989).

**6.** D. A. Parthenopoulos and P. M. Rentzepis, *Science* **245**, 843 (1989).

**7.** D. A. Parthenopoulos and P. M. Rentzepis, *J. App. Phys.* **68**, 5814 (1990).

**8.** A. S. Dvornikov and P. M. Rentzepis, *Opt. Comm.* **119**, 341 (1995).

**9.** W. Denk, J. H. Strickler, and W. W. Webb, *Science* **248**, 73 (1990).

**10.** U. Kubitscheck, M. Tschödrich-Rotter, P. Wedekind, and R. Peters, *Journal of Microscopy* **182**, 225 (1996).

**11.** A. S. Dvornikov, P. M. Rentzepis, Opt. Comm.**136**, 1 (1997).

**12.** Strickler. J. H. and W. W. Webb, Optics Lett. **16**, 1780 (1991).

**13.** J. D. Bhawalkar, N. D. Kumar, J. Swiatkiewicz and P. N. Prasad, Nonlinear Optics (In Press).

**Fig.1**. Absorption and Fluorescence spectra of the AF240 doped polymer film before and after exposure to UV light.

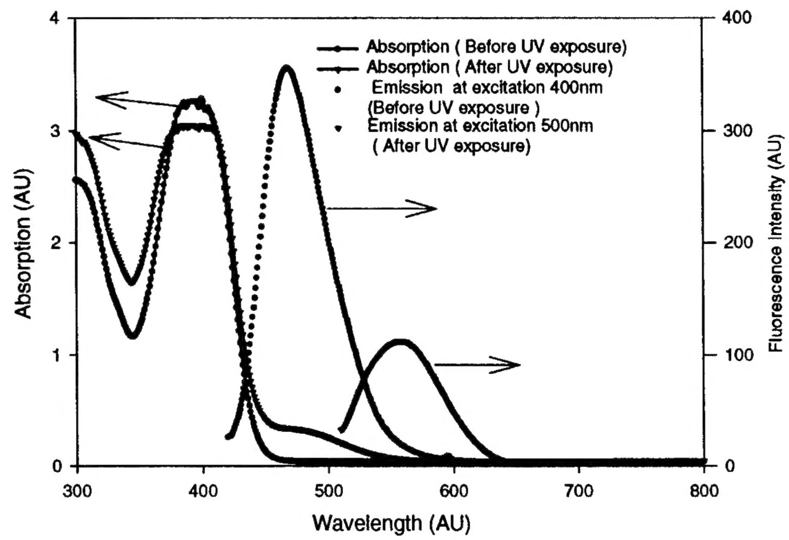
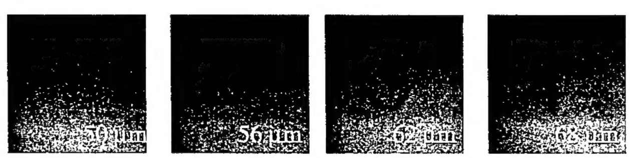



**Fig.2.** Two photon and single photon readback of multiple layers written at a spacing 6μm apart.

**Two photon read back of written layers**



**Single photon read back of written layers**

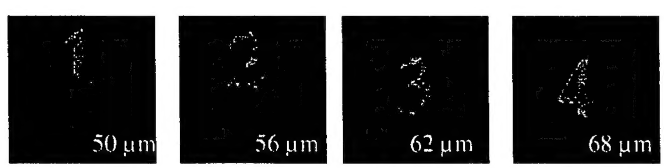


**Fig.3** Fluorescence intensity measured using X-Z scan profile of a written spot using confocal microscope, plotted against depth (a) in two photon readback and (b) in single photon readback.

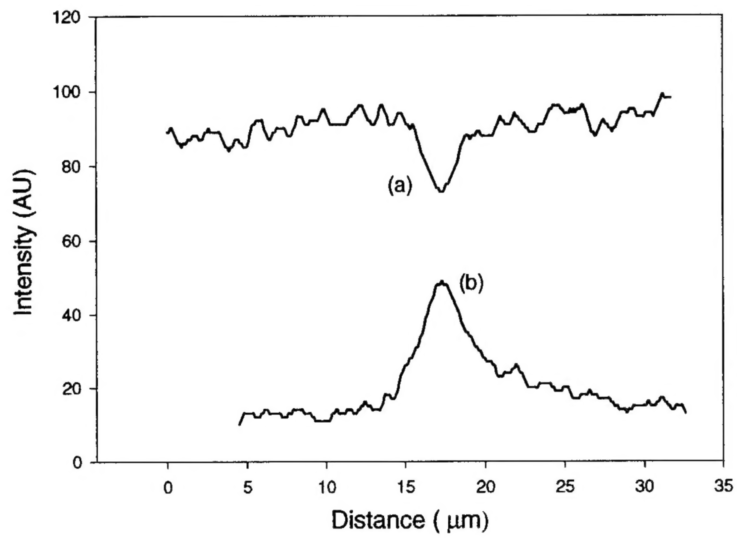
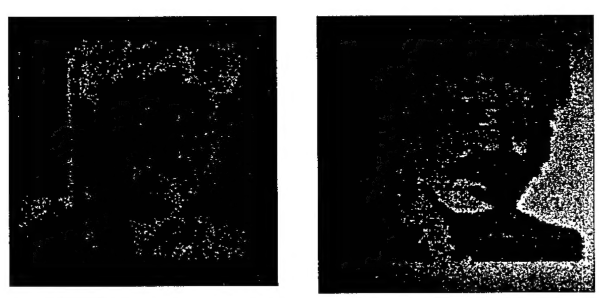



**Fig.4** Single photon and two photon readback of an image written using grayscale controll by changing the exposure time.



**Single photon read back** **Two photon read back**

Fig.5. An original photograph with Single photon and two photon readback from the written data

**Original Photograph**

**Single photon read back**

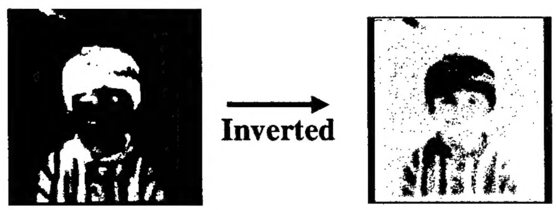



**Fig.6** An example of a three dimensional, multi-layer barcodes written in a polymer media.